

EXPERIMENTAL¹¹

2-Nitro-6-methoxytoluene. A solution of 2-methyl-3-nitrophenol^{4,5} (73 g.) in 400 ml. of water containing 19 g. of sodium hydroxide was cooled and treated with 60 g. of dimethylsulfate. The mixture was then stirred and heated on the steam bath for 2 hr. before subjecting the crude reaction mixture to a steam distillation. The cream colored product was collected with ca. 6 l. of water; yield 42 g. (53%), m.p. 55–57.5°. Simonsen and Nayak¹² report a melting point of 52–53°.

2-Nitro-6-methoxybenzaldehyde (I). A solution of 2-nitro-6-methoxytoluene (40 g.) in 250 ml. of carbon disulfide was added over a 30 min. period to a stirred solution of chromyl chloride (70 g.) in the same solvent (150 ml.). After 72 hr. at room temperature, the dark colored crystalline intermediate was collected and washed with carbon disulfide. After adding the solid to water, the aqueous mixture was extracted with chloroform and the combined chloroform extracts washed with saturated sodium bicarbonate solution and water. Removal of solvent afforded 15 g. (35%) of crude red colored crystalline product. Four recrystallizations from carbon tetrachloride gave an analytical sample as colorless needles, m.p. 110–111°, λ_{CHCl_3} 5.85 μ .

Anal. Calcd. for C₉H₇NO₄: C, 53.04; H, 3.90; N, 7.73. Found: C, 53.44; H, 4.23; N, 7.87.

The product was found to be identical (mixture melting point and infrared comparison) with a specimen prepared by Ashley's² procedure.

Trans-2-nitro-6-methoxy- α -(3',4'-methylenedioxy-6'-bromophenyl)cinnamic acid (IIIa). A mixture of 2-nitro-6-methoxybenzaldehyde (2.0 g.), 3.06 g. of 6-bromohomopiperonylic acid (II),^{8–10} acetic anhydride (10 ml.), and triethylamine (1 ml.) was heated at reflux for 15 min. before cautiously treating the hot reaction mixture with 10 ml. of water. After cooling, the mixture was neutralized with saturated sodium bicarbonate solution and extracted with chloroform. Acidification of the aqueous solution with dilute hydrochloric acid yielded 0.87 g. (17%) of crude pale yellow product, m.p. 200–230°. Three recrystallizations from acetic acid–water afforded a pure sample as pale yellow crystals, m.p. 264–265° (dec.), λ_{KBr} 5.95 μ .

Anal. Calcd. for C₁₇H₁₂BrNO₇: C, 48.36; H, 2.87; N, 3.32. Found: C, 48.48; H, 3.03; N, 3.53.

Trans-2-amino-6-methoxy- α -(3',4'-methylenedioxy-6'-bromophenyl)cinnamic acid (IIIb). A suspension of IIIa (0.55 g.) in a solution composed of ferrous sulfate (3.3 g.), hydrochloric acid (0.2 ml.), and water (5 ml.) was heated to 90–95° before adding 3 ml. of 28% ammonium hydroxide. Heating on the steam bath and intermittent stirring were continued for 45 min. The hot reaction mixture was then filtered through Norit-A and after washing the filter cake with water the combined filtrate was acidified to pH 4.5 with hydrochloric acid. The gray colored crystalline product weighed 0.41 g. (81%) and melted at 160–164°. Three recrystallizations from methanol–water gave a pure sample of the amino acid as yellow needles, m.p. 205–206°, λ_{KBr} 5.95 μ .

Anal. Calcd. for C₁₇H₁₄BrNO₅: C, 52.07; H, 3.60; N, 3.57. Found: C, 52.04; H, 3.58; N, 3.62.

The amino acid was found to be virtually insoluble in dilute hydrochloric acid.¹³

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MAINE
ORONO, ME.

(11) All melting points were taken in open Kimble glass capillaries and are uncorrected. Elemental analyses were performed by The Microanalytical Laboratory of Dr. A. Bernhardt, Mülheim, Germany. The infrared spectra were determined by Mr. Evan Thomas of this department.

(12) J. L. Simonsen and M. Nayak, *J. Chem. Soc.*, 107, 828 (1915).

(13) Low solubility in dilute mineral acid has been encountered with other amino cinnamic acids. See for example: L. S. Hornig, *J. Am. Chem. Soc.*, 74, 4572 (1952).

Preparation of α,β -Unsaturated Sulfones

V. BALIAH AND M. SESHAPATHIRAO

Received November 26, 1958

In earlier papers^{1,2} from these laboratories it was reported that β -amino and α,β -unsaturated sulfones are formed when aryl- or alkyl-sulfonyl-acetic acids are condensed with aromatic aldehydes in the presence of ammonia in glacial acetic acid. The yields of the α,β -unsaturated sulfones in such condensations were found to be generally very low. Being engaged in studies on α,β -unsaturated sulfones we were interested in getting increased yields of these compounds. It has been found that the use of benzylamine in place of ammonia and refluxing the reaction mixture for a longer period reduce the β -amino sulfone in the product to a negligible amount and greatly increase the yield of the α,β -unsaturated sulfone. Even with catalytic amounts of benzylamine excellent yields of the unsaturated sulfones were obtained. Using this procedure many new unsaturated sulfones have been prepared (see Table I). In the same Table are shown the increased yields of the previously reported α,β -unsaturated sulfones.

EXPERIMENTAL

General procedure for the preparation of α,β -unsaturated sulfones. A mixture of the sulfonylacetic acid (0.1 mole), the aldehyde (0.1 mole), glacial acetic acid (25 ml.) and benzylamine (0.1–0.2 g.) was refluxed on a hot plate for 50 min. The product was cooled, mixed with 100 ml. of dry ether and set aside for 1 hr. In most cases the α,β -unsaturated sulfone, being sparingly soluble in ether, partly crystallized out. It was removed by filtration and dry hydrogen chloride was passed into the ether solution. The precipitated β -amino sulfone hydrochloride, if any, was filtered off. Evaporation of the ether from the filtrate gave a mixture of the unreacted aldehyde, acetic acid, and unsaturated sulfone. Treatment of this mixture with a few ml. of methanol or isopropyl alcohol precipitated the unsaturated sulfone in many cases. In other cases the unchanged aldehyde had to be removed with sodium bisulfite before the unsaturated sulfone could be separated. The relevant data on the compounds prepared are given in Table I.

Acknowledgment. The authors wish to thank the Government of India for the award of a Research Scholarship to one of them (M.S.).

ANNAMALAI UNIVERSITY
ANNAMALAINAGAR, INDIA

(1) M. Balasubramanian and V. Baliah, *J. Chem. Soc.*, 1844 (1954).

(2) M. Balasubramanian, V. Baliah, and T. Rangarajan, *J. Chem. Soc.*, 3296 (1955).